

SUSTAINABILITY OF NATURAL ATTENUATION IN CONTAMINATED AQUIFERS DEPENDS ON THE AVAILABILITY OF ELECTRON ACCEPTORS. I. M. Cozzarelli, U.S. Geological Survey, 431 National Center, Reston, VA 22092, icozzare@usgs.gov.

Introduction: Monitored natural attenuation is receiving attention as a remedial option for organic contaminants in aquifers [1]. Intrinsic bioremediation, one aspect of natural attenuation that uses the *in situ* microorganisms to degrade contaminants, has received attention because the contaminants are degraded to less harmful products without using costly engineered systems. Studies have shown that the dominant microbial processes change over time in the anoxic plumes that typically develop downgradient from point-source contamination, resulting in different rates of degradation of organic compounds. For example, the depletion of reducible solid iron-oxyhydroxides in narrow zones in anoxic aquifers has allowed sulfate reduction (e.g. at Galloway, NJ [2]) or methanogenesis (e.g. at Bemidji, MN [3], [4]) to occur at small spatial scales. Thus, the availability of alternate electron acceptors is an important factor for evaluating the efficacy and sustainability of intrinsic bioremediation.

Studies at Norman Landfill: Studies of natural attenuation at a closed municipal landfill in Norman, OK, indicate a downgradient contaminant plume with concentrations of dissolved organic carbon (DOC) as high as 200 mg/L has developed [5]. Within the core of the plume (Fig. 1) the non-volatile DOC shows little change, indicating that most of it is not efficiently mineralized. Degradation occurs at the boundaries of the plume where electron acceptors are available. Cycling of sulfate and iron and formation of methane are important biogeochemical processes that affect aquifer geochemistry. Although the core of the plume is strictly anaerobic and supports both sulfate reduction and methanogenesis, the edges of the plume support iron reduction and, to a greater extent, sulfate reduction, due to the increased availability of readily reactive electron acceptors at these boundaries.

Non-uniform availability of electron acceptors and mixing of the contaminant plume with oxygenated water at the plume boundaries have an impact on biogeochemical processes resulting in sharp concentration gradients in ground water. High rates of sulfate reduction near the water table are controlled by the rate of sulfate supply from sulfide oxidation. Within the plume sulfate reduction is limited by the availability of sulfate, which is supplied by the slow process of barite dissolution. Electron acceptor concentrations such as sulfate show a seasonal pattern. A large sulfate peak is observed at the water table at times of high recharge (Fig. 2). A maximum over 1000 mg/L appears in late spring/early summer and moves downward as freshwater enters above the high

sulfate layer. The peak then decreases dramatically during the dryer fall season, reappearing in late winter/early spring with recharge. Comparison of sulfate to chloride indicates that the plume was present over the entire sampled depth and the process of sulfate reduction, rather than the process of dilution, explains the loss of sulfate. This study demonstrates the importance of assessing the availability of electron acceptors in both the aqueous and solid phases as well as at the appropriate spatial and temporal scales when developing conceptual models of the potential for contaminant transport in anoxic aquifers.

References: [1] Bekins B. A. et al. (2001) *EOS Transactions*, 82, 53–58. [2] Cozzarelli, I.M., et al. (1999) *J. Contam. Hydrol.* 40, 261–284. [3] Bekins, B.A. et al. (in press) *J. Contam. Hydrol.* [4] Cozzarelli, I.M., et al. (in press) *J. Contam. Hydrol.* [5] Cozzarelli, I.M., et al. (2000) *ES&T*. 34, 4025–4033.

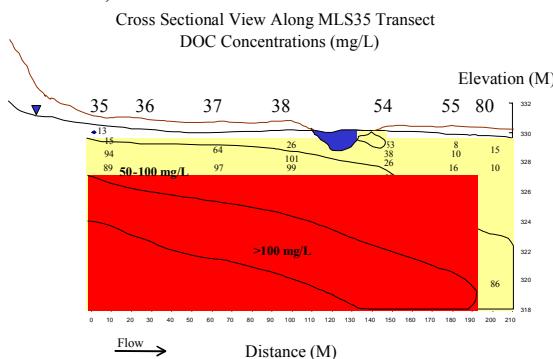


Figure 1. DOC in groundwater in 1997, along a transect downgradient from the landfill. Sites 35 – 80 are the locations of multilevel samplers

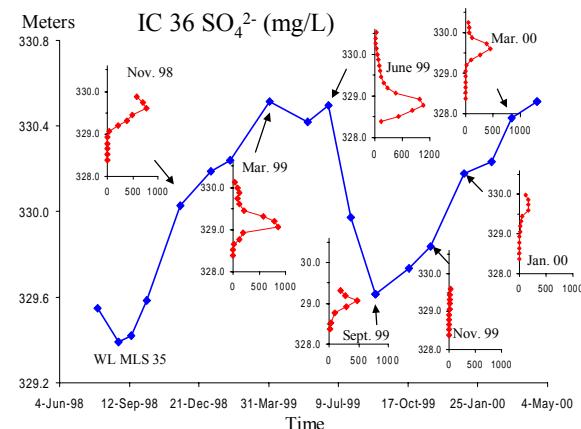


Figure 2. Water level vs. time in a well located in the contaminant plume plotted along with the concentrations of sulfate collected from closely spaced vertical samplers located at the water table.